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Robert Almqvist

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Robert Almqvist

Supervisor	Harald Cederlund, Swedish University of Agricultural Sciences, Department of Molecular Sciences
Assistant Supervisor:	Matthew Riddle, Swedish University of Agricultural Sciences, Department of Soil and Environment
Examiner:	John Stenström, Swedish University of Agricultural Sciences, Department of Molecular Sciences

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Foreword

The writer of this thesis wishes all the best and a great thank you to the two supervisors who were the foundation of this project. Great thanks goes to the examiner and a handful of people for supporting the project during its lapse of time. Kind wishes and a great thank you to the Biocentrum department at SLU Uppsala, for applying resources and equipment to make the experiment possible.

Abstract:

Nutrients in leachate water resulting from manmade activities are recognized as a major problem leading to eutrophication worldwide. In Sweden and other Baltic countries, agricultural activities are a big contributor to eutrophication of the Baltic Sea. In order to eliminate these problems, different techniques have been trialled over the years with mixed results. One method using magnetite biochar has been explored due to its adsorption properties allowing it to attract negatively charged chemical ions such as phosphate in leachate water. Biochar itself has a limited capacity to attract phosphate via surface-surface molecular interaction, but chemical treatment of plain biochar can change its chemical behaviour. The main objective of this present experiment was to determine the adsorption properties of magnetite biochar as a phosphate mitigation tool in a laboratory study. Biochar, "*Skogens kol*", was treated with an iron(II) /iron(III)-mixture resulting in formation of an iron oxide, magnetite, on the biochar surface. Adsorption experiment results revealed the magnetite biochar adsorbed twenty times as much phosphate in comparison to the non-treated biochar, where adsorption was little. A follow up column leaching experiment showed that the 285 kg ha^{-1} phosphate application rate had accumulated an additional ± 5.6 mg PO_4 and the 570 kg ha^{-1} application rate ± 9.3 mg PO_4 for columns containing magnetite biochar in comparison to columns containing only sand, indicating adsorption at the magnetite biochar. In the column experiment the total contact time between the biochar and the phosphate, < 10 hours because of high water application rate (0.3 mL min^{-1}), was lower in contrast to the adsorption experiment (24 hours) and is therefore suggested as a main contributor to the differing results.

Both the adsorption and column leaching experiments showed distinct adsorption abilities when using the Fe-coated biochar in comparison to the control. The results suggest that application of Fe-coated biochar as a phosphate mitigation tool has potential for commercial application. However, further research on the importance of contact time between phosphate and the char, pH conditions and stability of the biochar's adsorption properties over time is suggested.

Contents

1. Introduction:

Anthropogenic phosphorus (P) losses from agriculture is one of the major sources contributing to eutrophication in local lakes and seawater worldwide (Persson et al., 1994). Most phosphorus that reaches surface waters originates from arable land. Arable soils have varying phosphorus adsorption potential properties depending on soil characteristics. Generally, the more weathered a soil is, the greater the phosphorus adsorption, with the presence of non-crystalline oxides of iron and aluminium, phosphate molecules can be fixed (Persson et al., 1994). However, this is less relevant for Swedish soils that are relatively young and un-weathered. The annual leaching of phosphorus in Swedish soils have been measured at 0.4 kg P ha^{-1} which is sufficient to cause eutrophication in surface waters (Bergström et al., 2008). The minimum phosphate concentration recognized to cause eutrophication is 0.02 mg L^{-1} (Yao et al., 2013).This present study focused on using biochar as an adsorbent for phosphorus in soil solution. Biochar is obtained when organic matter, such as wood, manure or leaves, are pyrolyzed, which is the process of heating with restricted oxygen infusion. Adding untreated biochar to highly weathered oxisol soils adds soil quality and decreases the leaching rate of a majority of soil nutrients (Major et al., 2012). Using biochar as soil amendment in temperate soils has also been shown to contribute to decreasing nutrient leaching in a 45 week leaching experiment (Laird et al., 2010). Columns containing untreated biochar released significantly less nitrogen and P than those without biochar, although the biochar itself added additional nutrients into the soil mass. Biochar is a rather non-reactive, negatively charged organic compound (Hollister et al., 2013). However, studies of biochar soaked in solutions of iron (Fe^{3+}/Fe^{2+}) and pyrolysis at different temperatures, 250 °C, 400 °C and 700 °C have been shown to precipitate magnetite on the biochar's surface (Chen et al., 2011). This presents a platform allowing complex adsorption of phosphorus biomolecules (Chen et al., 2011). Another experiment of phosphatation on magnetite nanoparticles has demonstrated that these particles give notable adsorbent properties in comparision with more common iron hydroxides, such as the mineral goethite

(Daou et al. 2007). Further characterization of the phosphatation has shown that the iron to phosphate interaction occurs with Fe^{3+} on octahedral sites.

Our hypothesis for this study was that the untreated biochar would adsorb little to none of the phosphate, but the magnetite biochar with an increased cation presence, would adsorb more. The adsorbent properties of the magnetite biochar, if proved effective, would be of interest in commercial use in back-filling drainage trenches and surrounding surface water drain entries. Since the untreated char is rather unreactive, the primary focus of the experiment was to see if the properties of the Fe-coated biochar can improve adsorption of P under laboratory conditions. To enable this, the study was divided into three stages: i) Production of the iron (Fe^{2+}/Fe^{3+}) magnetite biochar, ii) an adsorption study and iii) a column leaching experiment.

2. Methods:

2.1 Coating biochar with magnetite

The biochar was coated following a procedure adapted from Šafařík et al. (1997) and Chen et al. (2011). Approximately 1 L of *Skogens kol* biochar was measured up and sieved through a < 4 mm sieve. The charcoal was put into two 500 mL conical flasks. Two different compounds, $FeCl_3$ x $6H_2O$

Figure 1: Rinsing process of the newly coated char; *Robert Almqvist 2017-02-15*

and $FeCl_2$ x $4H_2O$, 144 g and 53.1 g respectively, giving a ratio between iron(II) and iron(III) of 2:1, was added to the flasks. A reagent of 30% NaOH was used to precipitate the iron on the biochar. The three components, biochar, $FeCl_2$/$FeCl_3$ compounds and NaOH were added together in a 5 L conical flask. The components were mixed and heated for 1 h at 100 °C. After cooling, the mixture was filtered using 18 cm Ø No.3 Whatman paper (Fig. 1). The biochar was then rinsed with 2 L distilled water to remove any excess solution left on the biochar prior to drying. The biochar was then air dried in an oven at 50 °C for 24 h. The biochar was then sieved with a < 1 mm sieve into two different fractions, < 1 mm and between 1 and 4 mm fractions. These were then used in the following two experimental phases.

2.2 Adsorption experiment

A 500 mg L^{-1} phosphate stock solution (0.01614 mol L^{-1}) was made from both KH_2PO_4 and K_2HPO_4 in a 1000 mL volumetric flask adjusted to pH 6.5 using KOH. Concentrations of 0, 25, 50, 75, 100 and 250 mg PO_4 L^{-1} were diluted from the stock solution. An amount of 0.1 g of the < 1 mm magnetite biochar or untreated biochar was added to a 50 mL Sarstedt tube and mixed with 10 mL of one of the seven phosphate concentrations mentioned above. This procedure was replicated 5 times per concentration, giving 70 Sarstedt tubes in total, 35 for the magnetite-coated and 35 for the untreated biochar, respectively.

Figure 2: Filtrating using Plastipak syringes; *Robert Almqvist 2017-03-09*

The tubes were shaken horizontally for 24 hours at 200 rpms on a shaking table. After shaking, the tubes were centrifuged on a Jouan CR322 tabletop centrifuge. Samples were then filtered using Plastipak syringes with Ø 0.45 µm filters into 15 mL scintillation vials (Fig. 2). A new syringe was used for each phosphorus concentration, while the filter disks were replaced after each sample. Samples were labelled and chilled at 3 °C until analysed. The total phosphate content of the samples was determined colorimetrically by flow

injection analysis (FIA) using a FIAstar 5000 (FOSS, Hilleroed, Denmark). The method used in this case being AN 5241. Prior to analysis, samples were diluted to fit the calibration range (0.1 mg L^{-1} – 5 mg L^{-1}). All samples were diluted to 1:100 apart from the highest concentration of 500 mg L^{-1}, which required further dilution to 1:125. Each sample was analysed twice, and the mean value was used for the further data treatment. The standard solution of the original six different phosphate concentrations 25, 50, 75, 100, 250 and 500 mg P L^{-1} were also analysed. Two replicates were made of each concentration, thus giving 12 samples. Initial pre-tests revealed the amount of phosphate in dilutions differed from the nominal concentrations. Analysis instead indicated 26, 57, 89, 121, 294 and 553 mg P L^{-1} respectively. These concentrations were used instead of those calculated.

2.3 Column leaching experiment

The third phase of the project was to examine the adsorption properties of the treated biochar in a column leaching experiment. After observing negligible phosphate adsorption from untreated biochar in the previous experiment, the use of untreated biochar in the leaching experiment was

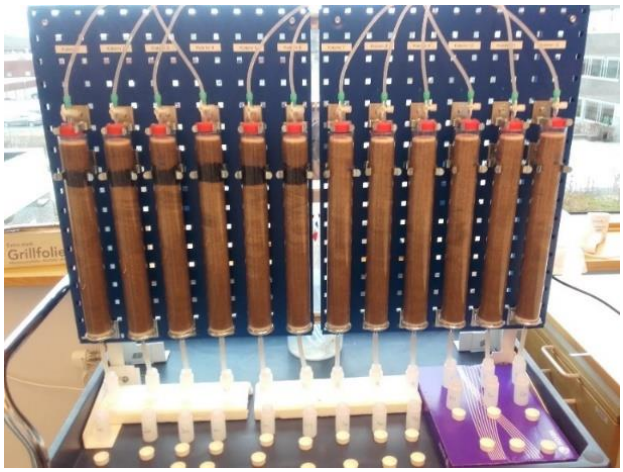

Figure 3: Columns containing sand and biochar; *Robert Almqvist 2017-03-29*

deemed unnecessary for this study. A series of twelve 35 cm long x 4 cm in diameter columns (Saveen & Werner AB, Limhamn, Sweden) were mounted on a moveable trolley. Clean sand (Ø = 0.5 mm; Rådasand AB, Lidköping,

Sweden) was used to fill each of the twelve cylinders. In six of the columns, a 3 cm layer of 1-4 mm biochar was placed 4 cm below the top of the sand. The non-biochar containing columns were filled with sand only (Fig. 3). A ceramic plate was laid on top of every column to aid in even water dispersal. The columns were then filled from the bottom up with deionized water a day before the leaching experiment took place using a peristaltic pump (IPC 12 (Labinett AB, Gothenburg, Sweden). Two replicates of three different phosphate concentrations were used in the leaching experiment. The initial amount of phosphate applied in the different columns were 2.96 mg P, 39.5 mg P and 79 mg P. These amounts were equivalent to 22, 285 and 570 kg PO_4 ha^{-1} if applied in a field scale. These were chosen based on the maximum rate of manure P application allowed on Swedish agricultural land every year, the maximum calculated adsorption capacity of the biochar and two-times the maximum adsorption capacity, respectively.

The flow rate of the leaching was set to 0.3 mL min^{-1} (14.4 mm h^{-1}). The leachate was collected every 40 min for 10 h giving a total of 180 samples (12 columns x 15 samples/column). Each sample was weighed and subsequently chilled at 3°C. The phosphate content of the last 12 samples of each column was analysed using FIA as described above.

3. Results and Discussion

The use of biochar as a phosphate adsorption method is based on adsorption occurring on the outer sites of the biochar, at the magnetite layer. The phosphate molecules are adsorbed by forming an assumed P-O-Fe link with the magnetite surfaces. A schematic, proposed illustration of how the iron-phosphate interaction occur on the magnetite biochar proposed by Daou et al. (2007) is shown in figure 4. Organic matter, including biochar, consists of a large amount of complex carbon molecule structures.

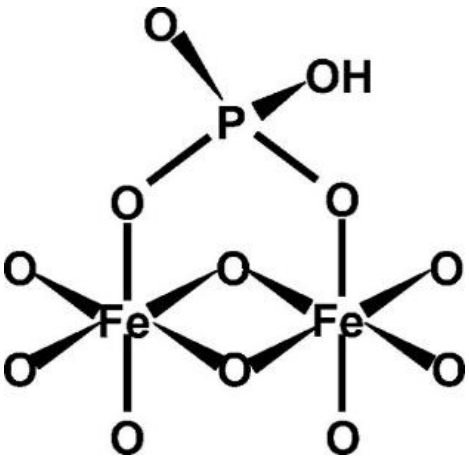

Figure 4: Phosphate and magnetite surface interaction. From Daou et al. (2007).

One of them being carboxyl groups (COO^-) which, un-protonated during certain conditions, forms an overall negatively charged outer surface of the organic matter (Eriksson et al. 2011). These chemical properties makes binding of negatively charged ions like phosphates unfavourable. The magnetite coating is seeming to act as a connecting link between the negatively charged biochar and the negatively charged phosphate ions, thus making adsorption for the magnetite biochar more advantageous. Based on the above assumption the hypothesis for this study was that the untreated biochar would adsorb little to none of the phosphate applied to the sample but the magnetite biochar would act the opposite, adsorbing a notable amount of it.

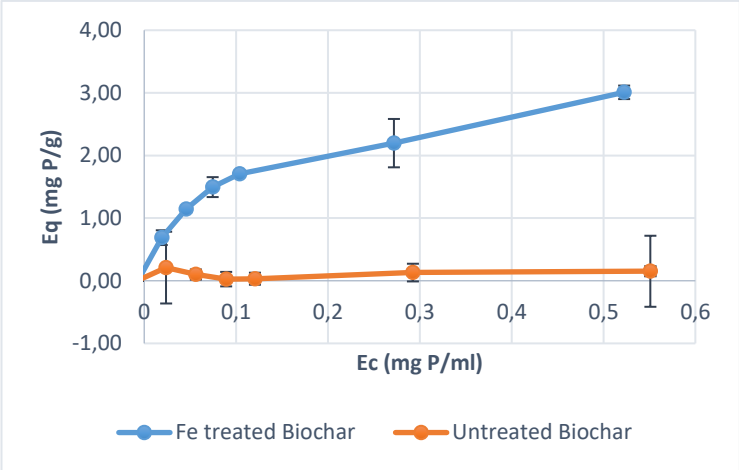

Figure 5: Adsorption isotherms for iron-treated and untreated biochars.

During the adsorption study, measurements were taken at all the six different phosphate concentrations. Figure 5 illustrates the adsorption isotherm of phosphate adsorption in the magnetite treated and untreated biochar. The maximum potential amount of phosphate capable of being adsorbed to the magnetite was estimated to be 3.38 mg PO_4 g^{-1} biochar by fitting a

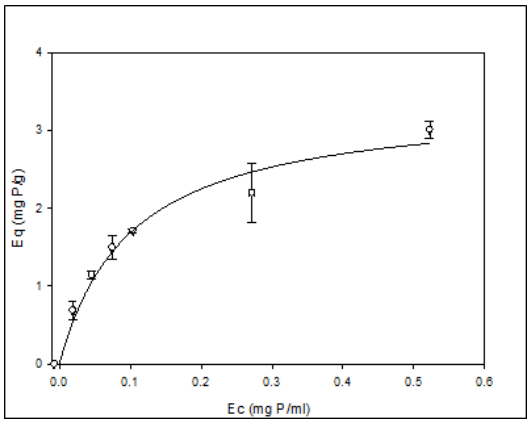

Figure 6: Langmuir isotherm of the magnetite biochar adsorption data

Langmuir isotherm to the data (Fig .6). The untreated biochar showed little to no adsorption of phosphate, as seen in figure 4, including evidence of phosphate release from the biochar. The complete list of concentration measurements are shown in supplementary tables 1 and 2. Results from a biochar study by Chen et al. (2011) showed adsorption capacities around four

times higher for the magnetite coated biochar than the untreated, at equilibrium concentration. A study of a nano-Cerium oxidized biochar exhibited as high as thirty times as high adsorption capacity in comparison to a plain biochar (Yanfang et al. 2017), which furthermore exhibits the notable adsorbent properties coating of plain biochar can have.

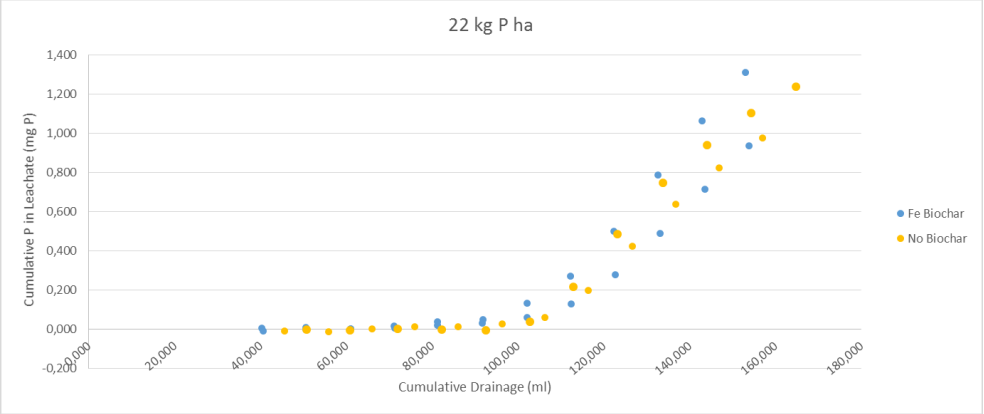

Figure 7: Cumulative phosphate amounts in leachate with 22 kg P ha application

A lower amount of phosphate was expected to reach the bottom of the leaching columns containing Fe-biochar in comparison to those without, at the same amount of cumulative drainage.

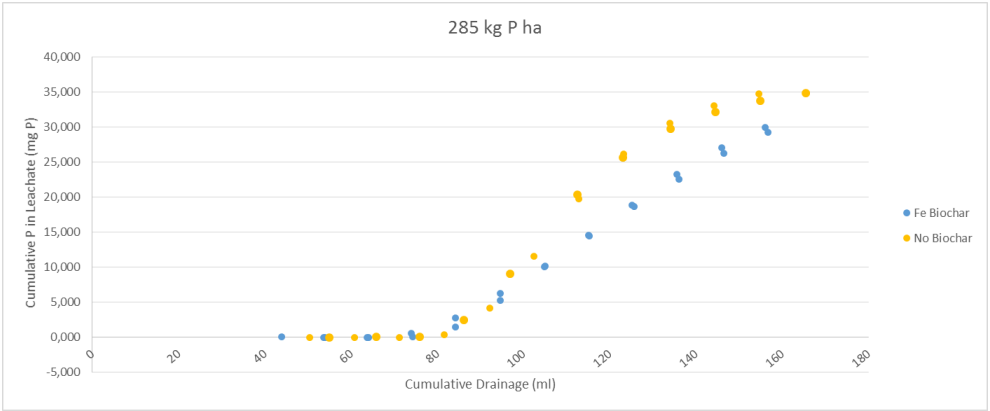

Figure 8: Cumulative phosphate amounts in leachate with 285 kg P ha application

The results revealed there was little difference in the amount of phosphate retained by the Fe treated biochar compared with the no biochar control at the lowest phosphate loads in the column study, as shown in figure 7. At the two

higher loads, 285 kg PO_4 ha^{-1} (Figure 8) and 570 kg PO_4 ha^{-1} (Figure 9), more phosphate was retained in the biochar treatment compared to the controls.

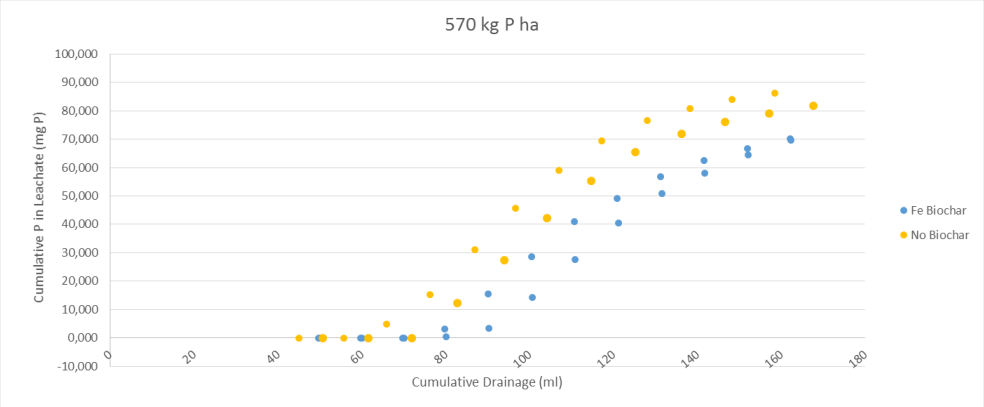

Figure 9: Cumulative phosphate amounts in leachate with 570 kg P ha application

3.1 Comparison of the different experiments and the impact on phosphate adsorption

The small contact time between the phosphate and the biochar in the column leaching experiment is one explanation for the reduced adsorption. During the leaching experiment, the flow of water was set to 0.3 mL min^{-1}. This would represent a rainfall as high as 14.4 mm $hour^{-1}$, which is a very high precipitation rate, considering a moderate rainfall would be approximately 0.5-4 mm $hour^{-1}$ and a heavy rainfall 4-10 mm $hour^{-1}$ (SMHI, 2015). Another suggestion for the difference between experiments is that the adsorption experiment was run for 24 h to reach equilibrium. This was a rather long time compared to the 10 h duration of the column experiment. The contact time of the biochar and the phosphate would also have been much lower than the 10 h, due to the high flow rate that was used in the column experiment. It would have been interesting to retest the biochar using a lower flow rate with a longer contact time with the phosphate. Amounts of phosphate adsorbed could then possibly have been notably higher. As can be seen in Supplementary table 2, it is not completely certain that the cumulative phosphate amount peaks at the last sample, taken 10 h after the leaching started. An additional amount of samples and running the experiment for a prolonged time would therefore also have been of interest.

Our results, as well as those of similar projects, indicate that the adsorption properties of the treated biochar have potential in a commercial situation. A Swedish study of a magnetite biochar for leftover pesticide adsorption also indicates the interest of using the properties of the magnetite biochar as a filter material, in a way that has, not extensively, been explored earlier (Cederlund et al. 2016). Whether the differing results from the two experiments were due to the current experimental conditions or if the treated biochar will prove to be less effective in phosphate adsorption during leaching conditions in the field remains to be seen. The results and discussion however, strongly supports the hypothesis of the improved adsorbent properties of the magnetite biochar.

4. Conclusion

A larger amount of the phosphate applied in the experiment was adsorbed by the magnetite biochar than the untreated biochar. A noteworthy amount of phosphate was also retained by the magnetite biochar during leaching conditions in the column experiment, however the amounts are lower than expected, probably due to the high flow rate used. With this experiment, it has been shown that biochar itself cannot adsorb a significant amount of phosphate in chemical surface-to-surface interaction. This study give data and information showing that the magnetite biochar has some chemical properties favourable for phosphate adsorption. However, although usage of a magnetite coating proved relatively effective, further research of other coating elements is of interest. Future investigations should focus more on the importance of pH, stability over time as well as how to practically apply the magnetite biochar in commercial use.

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Supplementary Data

Table 1: Phosphorus adsorbent amounts for untreated biochar

	Untreated Biochar			
Concentration (mg P L^{-1})	Equilibrium conc. (mg/L)	Standard dev.	Adsorbed amount Eq (mg/g)	Standard dev.
0	-7.73	0.48	0.00	0.00
26	23.87	0.39	0.21	0.57
57	56.20	0.81	0.10	0.08
89	89.19	1.16	0.03	0.12
121	120.50	0.96	0.03	0.10
294	292.52	1.41	0.13	0.14
553	551.06	5.67	0.15	0.57

Table 2: Phosphorus adsorbent amounts for Fe treated biochar

	Fe treated Biochar			
Concentration (mg P L^{-1})	Equilibrium conc. (mg/L)	Standard dev.	Adsorbed amount Eq (mg/g)	Standard dev.
0	-6.97	0.83	0.00	0.00
26	19.08	1.18	0.69	0.12
57	45.76	0.48	1.14	0.05
89	74.49	1.59	1.50	0.16
121	103.76	0.25	1.71	0.03
294	271.85	3.86	2.20	0.39
553	522.49	1.08	3.01	0.11

Table 3: Phosphorus column leaching amounts table

Date	17.03.29	Column Leaching Experiment								Bottle and lid weight =			6,715 g	
		22kg + Bio	22kg + Bio	285kg + Bio	285kg + Bio	570kg + Bio	570kg + Bio	22kg only	22kg only	285kg only	285kg only	570kg only	570kg only	
	ml leachate	Treatment Number Weight including bottle and lid (g)												
Time		1	2	3	4	5	6	7	8	9	10	11	12	
Initial drainage		49,53	37,9	35,36	49,56	37,95	30,66	60,79	48,95	57,74	63,61	75,97	58,48	
742	a	10,205	10,865	14,115	13,635	19,695	19,565	16,235	20,555	17,495	21,145	11,915	19,765	
822	b	9,945	9,455	10,165	10,165	10,015	10,205	8,915	9,845	11,945	12,625	11,995	9,575	
902	c	10,095	10,155	9,785	9,865	10,015	10,245	10,145	10,115	10,505	10,485	10,505	10,635	
942	d	10,115	10,105	9,945	9,945	10,045	10,135	10,345	10,255	10,545	10,815	10,725	10,835	
1022	e	10,255	10,045	10,015	10,015	9,985	9,945	10,275	10,075	10,415	10,755	10,605	10,825	
1102	f	10,425	10,335	10,155	10,175	10,045	9,975	10,075	11,085	10,345	10,165	10,205	10,405	
1142	g	10,235	10,115	10,115	10,165	10,065	10,045	9,945	10,285	10,365	10,285	10,285	10,835	
1222	h	9,965	10,125	10,035	10,245	10,245	10,175	10,175	10,345	10,635	10,615	10,705	11,185	
1302	i	10,565	10,535	10,365	10,485	10,355	10,345	10,225	10,245	10,255	0,085	9,825	10,145	
1342	j	10,265	10,395	10,285	10,355	10,305	10,255	9,985	10,035	10,365	15,505	10,345	10,535	
1422	k	10,155	10,235	10,105	10,285	10,185	10,275	9,995	10,335	10,355	10,615	10,145	10,435	
1502	l	10,145	10,345	10,175	10,335	10,395	10,435	10,395	10,685	10,845	11,055	10,845	11,095	
1542	m	10,195	10,425	10,345	10,395	10,325	10,235	9,985	10,285	10,195	10,365	10,115	10,445	
1622	n	10,295	10,365	10,355	10,455	10,285	10,305	10,215	10,275	10,375	10,385	10,125	10,395	
1702	o	10,185	10,345	10,165	10,295	10,275	10,255	10,125	10,415	10,305	10,585	10,095	10,565	
	Total (ml)	153,045	153,845	156,125	156,815	162,235	162,395	157,035	164,835	164,945	165,485	158,435	167,675	
(aim 130mm)	Total (mm)	110,46652	111,04396	112,68964	113,18768	117,09978	117,21527	113,34647	118,97644	119,05584	119,4456	114,35698	121,02633	